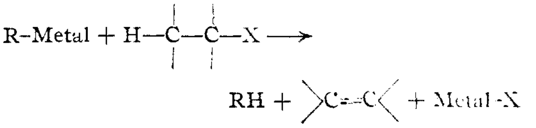
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Reactions of Organometallic Compounds. I. The Rates of Reaction of Phenyllithium and of Methyllithium with *n*- and *t*-Butyl Chlorides[1]

BY STANLEY J. CRISTOL, JAMES W. RAGSDALE AND JOHN S. MEEK

Although Ziegler and Colonius,[2] in one of their early papers on organolithium compounds, measured the half-lives of the reactions of butyllithium and *n*-butyl chloride, bromide and iodide in benzene and in ethyl ether at room temperature, they did not measure the order of the reaction. The reactions between organolithium compounds and alkyl halides (coupling or elimination) are of interest because of similarities to the second part of the postulated path for the Wurtz–Fittig reaction.[3,4,5,6]

$$\text{R–Metal} + \text{R}'\text{X} \longrightarrow \text{R–R}' + \text{Metal–X} \quad (1)$$



$$\text{R–Metal} + \text{H—}\overset{|}{\underset{|}{\text{C}}}\text{—}\overset{|}{\underset{|}{\text{C}}}\text{—X} \longrightarrow \text{RH} + {>}\text{C=C}{<} + \text{Metal–X} \quad (2)$$

We have found only one report[7] of a study of the kinetics of the reaction of an organolithium compound with an organic halide. These workers studied the reaction of phenyllithium with ω-chlorostyrene in ethyl ether at 0 and 20°, the over-all reaction being

$$C_6H_5CH{=}CHCl + 2C_6H_5Li \longrightarrow C_6H_5C{\equiv}CLi + 2C_6H_6 + LiCl \quad (3)$$

The expected second-order rate constants were not observed, but showed a large downward drift; the data could be accommodated to a third-order rate equation, first order in styryl chloride and second order in phenyllithium. Wittig and his co-workers proposed a complex mechanism for this elimination reaction to accommodate the third-order kinetics. The authors did not, however, seem to consider the purity of their styryl chloride, that is, no mention was made as to whether the halide was *cis* or *trans* or a mixture of the two. As elimination from *cis* and *trans* isomers may differ considerably in rate,[8,9] there seems to be a possible question as to the interpretation of Wittig's work, as the presence of a mixture would, of course, lead to a downward drift in second-order rate constants.

We have undertaken a study of the kinetics and of the products of the reactions of phenyllithium and of methyllithium with *n*-butyl chloride and with *t*-butyl chloride. These halides were chosen to give examples of primary and tertiary alkyl radicals; chlorides were chosen to minimize exchange reactions.[10] The reactions were run in di-*n*-butyl ether rather than ethyl ether to minimize handling difficulties at the temperatures required (50–100°) for reaction. The first experiments were conducted in volumetric flasks from which aliquots were withdrawn from time to time; better reproducibility was obtained by running the reactions in sealed tubes, and most of the data herein reported were obtained in this fashion.

The stoichiometry of the reactions was studied under conditions similar to those used in the rate measurements. In each case one mole of organometallic compound was consumed per mole of alkyl halide, but the reagents differed with regard to the relative amounts of substitution (coupling) and elimination produced. We were able to isolate 82–91% of the expected products of substitution and elimination, which suggests that these are the only processes necessary to consider. At 97°, phenyllithium and *n*-butyl chloride gave 84% recovery of *n*-butylbenzene (coupled product) and 3.8% recovery of 1-butene; with *t*-butyl chloride, no substitution occurred, but 87.5% of the expected isobutylene was obtained. At 88°, methyllithium reacted in a similar fashion with *t*-butyl chloride, giving 82% of isobutylene, but also gave predominant elimination with *n*-butyl chloride, 77% of 1-butene and only 14% of *n*-pentane, being isolated.

Solutions of phenyllithium in dibutyl ether were prepared by first preparing the organolithium compound from bromobenzene and lithium in ethyl ether.[11] The ethyl ether was then replaced by butyl ether.[12] After the solution had been filtered through glass wool and dried asbestos, the yield of phenyllithium (based on titration with acid) was 75–90%. Yields were very poor when bromobenzene was treated directly with lithium in butyl ether. The methyllithium solutions were prepared in ethyl ether from methyl iodide and lithium. Although the yield of methyllithium was good (over 80%) after formation in ethyl ether, replacement by butyl ether lowered the yield to 14–56%. All of the work was conducted under nitrogen with the usual precautions required for work with organometallic compounds.

Determination of Reaction Rates.—Solutions were prepared by placing a measured amount of standardized organolithium solution and a known quantity of butyl chloride in a volumetric flask, dry *n*-butyl ether was added to fill the flask, and the solution was then mixed thoroughly. Aliquots of this solution were then transferred to soft-glass test-tubes which had been previously drawn out, dried and flushed with nitrogen. The transfers were made with pipets that had been modified to make them fast-flowing and then recalibrated. A clean pipet was used for each sample. The tubes were sealed in a flame. The transfers were made as rapidly as possible and with as much nitrogen flushing as conveniently

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(1) This work was supported by the Office of Naval Research.

(2) Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

(3) Morton and Richardson, THIS JOURNAL, **62**, 123 (1940).

(4) Morton, Davidson and Hakan, *ibid.*, **64**, 2242 (1942).

(5) Whitmore and Zook, *ibid.*, **64**, 1783 (1942).

(6) Wittig and Witt, *Ber.*, **74B**, 1474 (1941).

(7) Wittig, Harborth and Merkle, *ibid.*, **77B**, 315 (1944).

(8) Chavanne, *Bull. soc. chim. Belg.*, **26**, 287 (1912).

(9) Cristol, THIS JOURNAL, **69**, 338 (1947).

(10) Langham, Brewster and Gilman, *ibid.*, **63**, 545 (1941).

(11) Gilman, Zoellner and Selby, *ibid.*, **55**, 1252 (1933).

(12) Coleman and Brooks, *ibid.*, **68**, 1620 (1946).

possible, but air was not rigorously excluded. The reactions were conducted in a constant-temperature oil-bath. Temperature control was probably within ±0.05°.

During the course of a run seven to nine such samples were withdrawn from time to time and quenched by cooling in ice or cold water. The tubes were broken into a flask containing ethanol and the solution titrated against standard 0.1 *N* hydrochloric acid, using lacmoid as indicator. For the runs with *t*-butyl chloride, absolute ethanol was used as solvent to minimize the solvolysis of the tertiary halide.[13] Blank tubes containing only the organolithium compound in ether, with halide absent, were also run as controls. It was observed that only a small percentage of the base disappeared in the time required for a run. Although this could have been neglected, the amount used in the control was subtracted from the run sample to give the value used. Although titration for total base does not necessarily indicate the correct titer for organolithium present, our use was justified by the isolation of *n*-butylbenzene in almost quantitative yield, and by a check run with methyllithium using the Zerewitinoff procedure (gas analysis for methane), which gave results consistent with those by the base-titration technique.

Calculation of Rate Constants.—The reactions studied were found to be of the second order—first order in organolithium compound and first order in alkyl halide—as the data could be accommodated to the form of the second-order equation

$$d \log \frac{1 - a\phi/b}{1 - \phi}/dt = \frac{b - a}{2.303} k \qquad (3)$$

connecting initial halide concentration *a*, initial phenyllithium concentration *b*, fraction ϕ of halide consumed and time *t*. The concentrations were corrected for the expansion of solvent from room to reaction temperature.[14]

Values of $\log (1 - a\phi/b)/(1 - \phi)$ corresponding to the various samples of a run were plotted as ordinates against corresponding values of time and the best straight line was drawn by inspection through the points. The slope of this line was multiplied by the value of $2.303/(b - a)$ for the run to give the rate constant *k*. This method for calculating the rate constant does not give undue weight to the first analysis made, nor is the value of *k* affected by uncertainties involved in the time taken as the start of the reaction. Typical treatments of the data are shown in Figs. 1 and 2, which are plots of four runs with the various reagents. The data and results are summarized in Tables I and II.

In general, satisfactory straight lines corresponding to the second-order rate equation were obtained over the intervals studied from the start of the reaction to from 30 to 75% completion. In a number of runs an autocatalysis seemed to be exhibited starting at 60–80% reaction. In these cases initial rate constants gave good agreement. In preliminary experiments with phenyllithium and *s*-butyl chloride (which reacted slower than the other two halides initially), marked autocatalysis was observed, starting at approximately 20% reaction, and reproducible rate constants were thus difficult to obtain. That the autocatalyst was not lithium chloride was shown by addition of

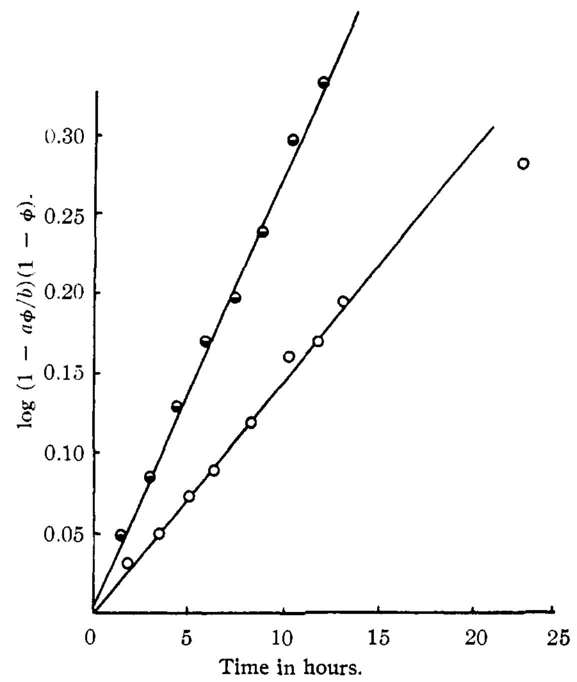

Fig. 1.—Treatment of rate data for phenyllithium, 0.339 *M*, and *t*-butyl chloride 0.124 *M*, ◒—◒; for phenyllithium, 0.155 *M* and *n*-butyl chloride 0.044 *M*, O—O; temperature, 79.98°.

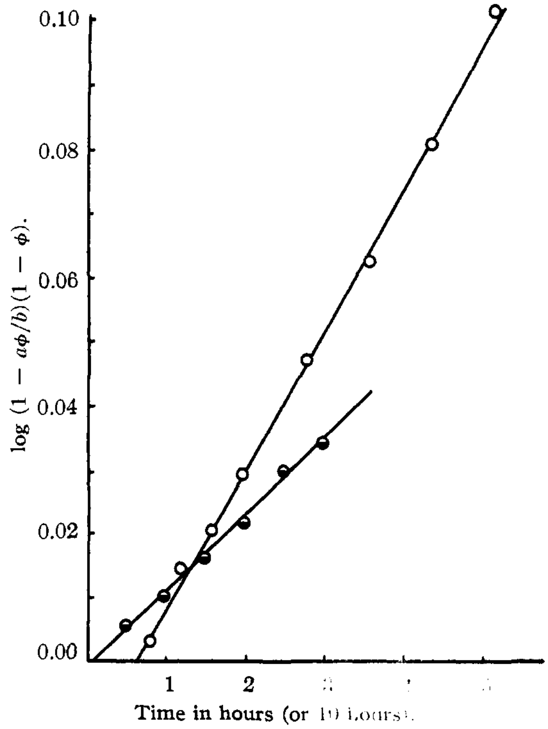

Fig. 2.—Treatment of rate data for methyllithium, 0.1[illegible]1 *M*, and *t*-butyl chloride, 0.127 *M*, ◒—◒, time scale in hours; for methyllithium, 0.161 *M*, and *n*-butyl chloride, 0.090 *M*, O—O, time scale in 10 hours; temperature, 78.85°.

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[13] Hughes, *J. Chem. Soc.*, 255 (1935).

[14] Bingham and Spooner, *J. Rheology*, **3**, 221 (1932).

TABLE I

DATA AND RESULTS FOR REACTION RATE CONSTANTS FOR REACTION OF PHENYLLITHIUM WITH *n*- AND *t*-BUTYL CHLORIDE

Halide	Temp., °C.	[Halide] *a*, *M*	[PhLi] *b*, *M*	Rate constant, $10^5 k$, l./sec./mole	Av.	Av. dev., %
n-Bu	48.9	0.205	0.412	0.296	0.319	7.2[a]
		.195	.588	0.342		
	62.51	.0905	.226	1.33	1.31	1.1
		.0905	.226	1.30		
	79.98	.131	.311	5.57	5.28	5.3
		.044	.155	4.82		
		.131	.308	5.23		
		.136	.339	5.50		
	97.40	.133	.331	21.0	24.8	11.0
		.044	.138	26.4		
		.133	.403	23.0		
		.133	.282	23.6		
		.133	.280	30.0		
t-Bu	48.9	.205	.412	0.426	0.386	10.6[a]
		.195	.588	0.345		
	62.51	.0905	.226	1.72	1.69	1.8
		.0905	.226	1.66		
	79.98	.124	.311	8.81	8.46	2.7
		.124	.308	8.46		
		.124	.339	8.11		
	97.40	.124	.331	39.4	40.9	5.4
		.124	.403	37.9		
		.124	.282	43.4		
		.124	.280	42.7		

[a] Run in volumetric flasks rather than sealed ampoules.

the amount of lithium chloride representing complete reaction to each tube. No significant difference was noted in the runs with and without added lithium chloride (see Fig. 3). Data on the secondary halide are not recorded herein in view of these peculiar results.

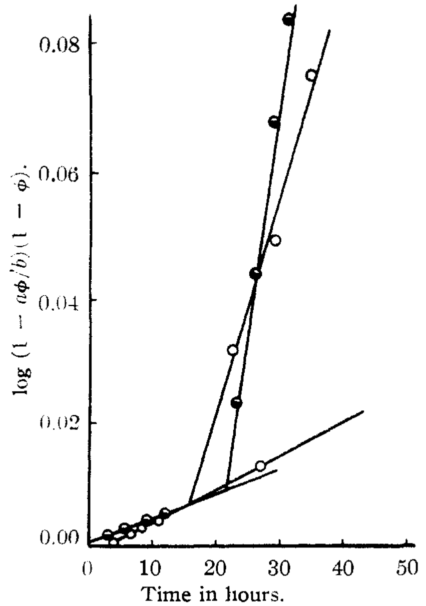

Fig. 3.—Treatment of rate data for phenyllithium, 0.335 *M*, and *sec.*-butyl chloride, 0.132 *M*, without added lithium chloride, O—O; with added lithium chloride, ●—●; temperature, 79.98°.

TABLE II

DATA AND REACTION RATE CONSTANTS FOR REACTION OF METHYLLITHIUM WITH *n*- AND *t*-BUTYL CHLORIDES

Batch of Me-Li	Halide	Temp., °C.	[Halide] *a*, *M*	[MeLi] *b*, *M*	Rate constant, $10^5 k$, l./sec./mole	Av.	Av. dev., %
I	*n*-Bu	78.87	0.136	0.195	3.97	3.92	1.3
			.0905	.195	3.86		
		88.92	.0894	.194	8.20	8.87	7.5
			.134	.194	9.54		
II		88.92	.0885	.232	4.76	4.33	6.7
			.0885	.156	4.32		
			.0442	.161	3.90		
		78.85	.0895	.161	1.92	2.02	4.9
			.134	.161	2.12		
		73.34	.0900	.165	1.33	1.33	
III		73.34	.0450	.0983	8.10	8.10	
IV		73.00	.0450	.0912	3.48	3.48	
I	*t*-Bu	78.87	.127	.195	38.9	37.8	2.9
			.0846	.195	36.7		
		88.92	.0836	.194	107.	107.	
II		88.92	.0835	.232	47.5	46.6	3.9
			.0835	.161	48.4		
			.0417	.161	43.8		
		78.85	.0844	.161	19.6	20.2	2.9
			.127	.161	20.8		
		73.34	.0849	.165	12.7	12.7	
III		73.34	.0425	.0983	72.5	72.5	
IV		73.00	.0425	.0912	26.5	26.5	

The data in Table I show the degree of reproducibility of the second-order reaction-rate constants with phenyllithium. We consider these results as satisfactory, in view of the difficulty of handling solutions of organometallic compounds and the fact that air was not rigorously excluded. The rate constants fit well to an activation energy curve (Fig. 4), indicating the self-consistency of the data.

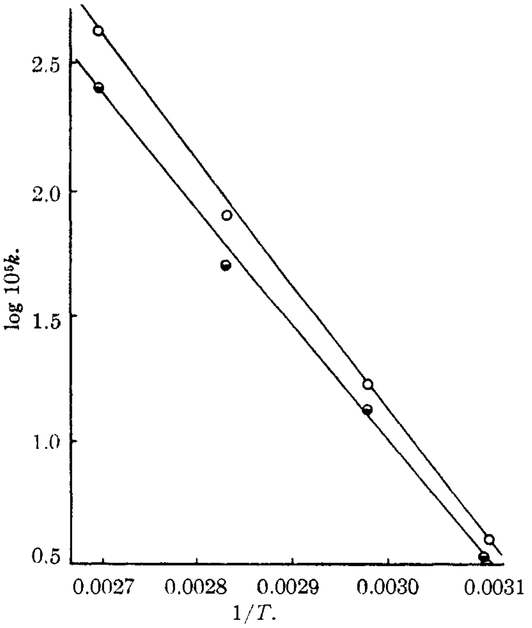

Fig. 4.—Plots for calculation of activation energies for phenyllithium and: O—O, *t*-butyl chloride; ●—●, *n*-butyl chloride.

The reaction of phenyllithium with *n*-butyl chloride in butyl ether to give *n*-butylbenzene proceeds with an activation energy of 21.2 kcal./mole; that with *t*-butyl chloride to give benzene and isobutylene proceeds at a rate 1.6 times faster than with the primary chloride at 80°, but with an activation energy of 22.7 kcal./mole.

The data with methyllithium were rather peculiar. Each run gave good agreement with the second-order rate equation and consistent with other runs using the *same preparation* of methyllithium; however, different batches of methyllithium gave rate constants differing from each other by as much as one order of magnitude. What catalyst was present in the various preparations is not known. Only one batch was prepared in a sufficiently large quantity for the estimation of activation energies. This was Batch II, where data at three temperatures are available. The plots of log *k* *vs.* $1/T$ are given in Fig. 5, and the data show good consistency. The reaction of methyllithium with *n*-butyl chloride gives a mixture of elimination and substitution, hence the calculated value of the activation energy of 18.9 kcal./mole has no precise meaning. The reaction of methyllithium with *t*-butyl chloride to give methane and isobutylene proceeds at a rate approximately ten times faster than the total second-order reaction with the primary chloride at 80°, but with a higher activation energy of 20.8 kcal./mole.

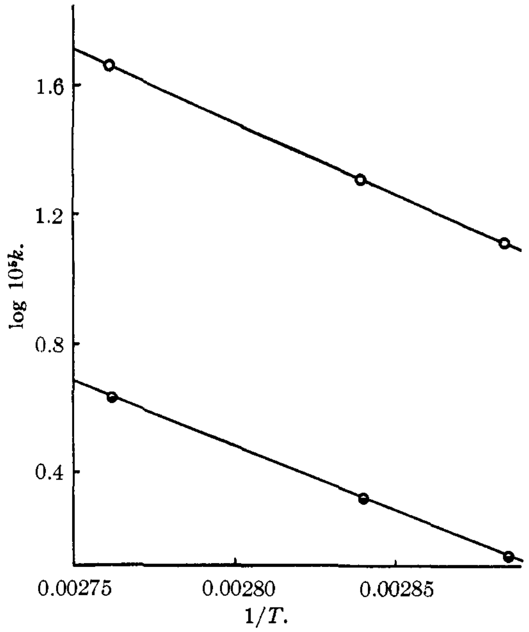

Fig. 5.—Plots for calculation of activation energies for methyllithium (Batch II) and O—O, *t*-BuCl; ●—●, *n*-butyl chloride.

Summary

The reactions of phenyllithium and of methyllithium with *n*- and *t*-butyl chlorides in butyl ether have been studied. Phenyllithium gave principally *n*-butylbenzene with *n*-butyl chloride and isobutylene and benzene with *t*-butyl chloride, whereas methyllithium gave predominantly elimination with either halide. Kinetic data indicated that both the substitution and elimination reactions were first order in organolithium compound and first order in alkyl halide.

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Reactions of Organometallic Compounds. II. The Reactions of Phenyllithium and of *n*-Butyllithium with α- and γ-Methylallyl Chlorides[1]

BY STANLEY J. CRISTOL, WENDELL C. OVERHULTS AND JOHN S. MEEK

α- and γ-methylallyl chlorides were reacted with phenyllithium in ethyl ether to give substantially identical mixtures comprising 90–95% of crotylbenzene and 5–10% of α-methylallylbenzene. Analogous results were obtained with *n*-butyllithium. The results are interpreted in terms of a carbonium-ion process. It is suggested that the coupling reactions of alkyl halides with organometallic compounds and with sodium can be understood in terms of a duality of mechanism—that is, both direct and carbonium-ion displacement mechanisms are available for these systems.

Although the mechanisms of the coupling reactions of organosodium and organomagnesium compounds with alkyl halides have been studied in some detail, less work has been reported on analogous studies with organolithium compounds. The reactions between organolithium compounds and alkyl halides are of interest because of similarities to the second part of the postulated path for the Wurtz–Fittig reaction[2,3,4]

$$\text{R-Metal} + \text{R}'\text{X} \longrightarrow \text{R—R}' + \text{Metal-X} \quad (1)$$

In a previous paper[5] we showed that the reactions of phenyllithium and methyllithium with *n*-butyl and *t*-butyl chlorides in butyl ether were of the second order, first order with respect to organolithium compound and first order with respect to alkyl halide.[6] As these data can be accommodated to a direct displacement or to a carbonium-ion mechanism, further study of reactions of organolithium compounds with alkyl halides seemed warranted.

We have, therefore, undertaken a study of the products of the reactions of phenyllithium and of *n*-butyllithium with α-methylallyl (methylvinylcarbinyl) and crotyl (γ-methylallyl) chlorides.

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(1) This work was reported, in part, before the Division of Organic Chemistry at the Spring, 1950, Meeting of the American Chemical Society, Philadelphia, Pennsylvania.

(2) A. A. Morton and G. M. Richardson, THIS JOURNAL, **62**, 123 (1940); A. A. Morton, J. B. Davidson and B. L. Hakan, *ibid.*, **64**, 2242, (1942).

(3) G. Wittig and H. Witt, *Ber.*, **74B**, 1474 (1941).

(4) F. C. Whitmore and H. D. Zook, THIS JOURNAL, **64**, 1783 (1942).

(5) S. J. Cristol, J. W. Ragsdale and J. S. Meek, *ibid.*, **73**, 810 (1951).

(6) Reactions with *n*-butyl chloride gave coupling and elimination, whereas with *t*-butyl chloride only elimination was observed.